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THE FRICTION COEFFICIENTS OF LIQUIDS.

By Jitsusaburo Sameshima, Hideo Akamatu
and Toshizo Isemura.

Introduction.

When two solid surfaces are brought into contact and made to slide the one on the other, the friction force comes into play. The friction is generally lessened by the presence of a liquid film between the solid surfaces. If a solid body of weight W is made just to slide on a horizontal surface by means of a force F whose direction is parallel to the surface, then F/W is known as the coefficient of friction. Thus,

$$\frac{\text{Friction resistance}}{\text{Normal weight}}=\frac{F}{W}=\mu.$$

The friction coefficient may differ according to whether motion is imparted to the body at rest or whether the force F is required to keep the body in motion. In the former case the coefficient is known as the static friction coefficient while in the latter as the kinetic friction coefficient.

Although a large number of investigators have published data bearing on the subject of lubrication, most of them conducted their experiments on the standpoint of the practical application. Moreover, the variations in their operating conditions and the indefiniteness of the chemical nature of the liquids used thus prevented any correlation of their results.

In practice, there are two types of lubrication, complete or film lubrication in which the solid faces are completely separated by a thick film of an oil, and incomplete or boundary lubrication in which the faces are separated by a very thin film which may be sometimes only one molecule thick. The theory of complete lubrication is a problem in hydrodynamics, and outside the scope of the present investigation.

The friction coefficients of some chemically definite substances have been measured by W. B. Hardy and his collaborators[1)2)]. It seems necessary, however, to test their results and to extend the measurements, with the hope of finding

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1) W. B. Hardy and Coworkers, *Phil. Mag.*, 38, 32 (1919); 40, 201 (1920); *J. Chem. Soc.*, 127, 1207 (1925); *Proc. Roy. Soc.*, A100, 550 (1922); 101, 487 (1922); 104, 25 (1923); 108, 1 (1925); "*Collected Scientific Papers of Sir William Bate Hardy*", (Cambridge, 1936).

2) I. Doubleday, *J. Chem. Soc.*, 121, 2875 (1922); *Proc. Roy. Soc.*, A106, 341 (1924).

the relations between the friction coefficient and other properties, especially molecular constitutions of the liquids.

We have measured the boundary lubrications of chemically pure substances as well as mixtures of known compositions. The static and the kinetic friction coefficients have been measured by using several different methods, which were designed in our laboratory.[3][4][5] In the present paper one of the methods for measuring the static friction coefficient is described.

Experimental Procedure.

The apparatus is shown in Fig. 1. *A* is the glass or the metal plate of plane surface which is settled on a suitable stand. *B* is the slider with a convex

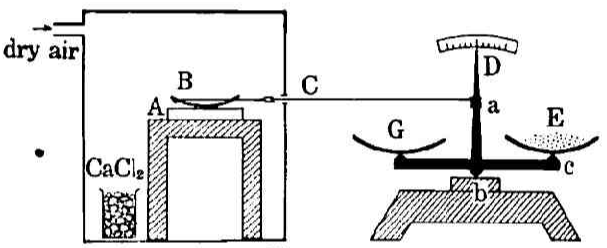

Fig. 1.

spherical surface, the radius of curvature of which is 6 cm. The weight of the slider is adjusted by putting lead shots on it. *C* is a thin copper wire, one end of which is hitched to the cutting of the slider *B*. The other end of *C* is connected with the middle part of the pointer *D* of a prescription balance.

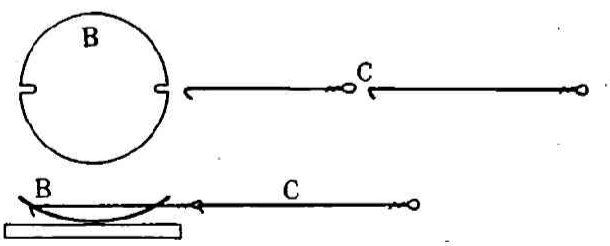

Fig. 2.

Fig. 2 shows the upper and the side views of *B* and *C*. *C* is made of two pieces of wire, short and long, each having a small hook at one end and a small

3) J. Sameshima and Coworkers, *Bull. Chem. Soc. Japan*, 11, 659 (1936); 11, 791 (1936); 12, 96 (1937); 12, 127 (1937).

4) H. Akamatu, *Bull. Chem. Soc. Japan*, 13, 127 (1938).

5) T. Sasaki, *Bull. Chem. Soc. Japan*, 13, 134 (1938).

ring at the other. The short piece is hitched to a cutting on the rim of the slider, and stretched out through another cutting opposite to the first one. The long piece is hooked to the ring of the short piece and to the pointer of the balance.

A and B are put in a glass case, provided with a vessel containing calcium chloride. A current of dry air is passed through the case during the observation to prevent the effect of moisture on the surfaces and the lubricating liquid. The lubricating liquid is poured on A and then the slider B is put on it. The position of the slider is adjusted so that the pointer D takes the upright position, the right and the left pans being balanced.

Now, fine sand is poured in a thin stream from a reservoir to the right pan E. The quantity of sand gradually increases until finally the right pan goes downward, the pointer inclines to the right side, and the slider A moves rightward. Then C is detached from D and the weight of the sand on the right pan E is measured by putting balance weights on the left pan G.

Let the weight of the sand be s, the length between a and b be l, and the distance between b and c be l', then the force acting on the slider is expressed by the following equation:

$$F=s\frac{l'}{l}.$$

So the coefficient of friction is obtained by

$$\mu=\frac{F}{W},$$

where W denotes the weight of the slider, i.e. the sum of the weight of slider, lead shots and one half of the wire C.

It was already known that the coefficient of friction is not seriously affected by the change of temperature[6]. We conducted, therefore, our experiments at room temperature without special adjustment of the temperature. In the experiments, we took the readings of the value s several times for a definite value of W, and then made their average. The value of l'/l was 1.22 or 1.23 for the balances used in the present measurements. The values of W varied between 10 and 40 grams.

It is a matter of the utmost importance that the sliding surfaces are sufficiently clean and entirely free from any greasy matter. The surfaces of glass and metal have been cleaned by the following methods.

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6) W. B. Hardy and I. Doubleday, *Proc. Roy. Soc.*, A101, 487 (1922).

The glass plate and the glass slider were boiled for half an hour with a chromic acid solution, washed and rubbed with the finger tip under the running tap water, and finally rinsed with distilled water. They were dried in a desiccator containing calcium chloride, a current of dry air being passed. No grease was applied on the ground part of the desiccator, to avoid the contamination of the glass surfaces.

Hardy and Doubleday[7] cleaned the surface of steel, for the measurement of friction coefficient, "by washing with soap and water, rubbing vigorously with the finger tip in a stream of tap water until water wetted the entire surface, rinsing with perfectly dry pure alcohol, and allowing to drain in air". We have tried this method for the cleaning of the surfaces of silver. But the result was not satisfactory for the surface from which water was repelled completely by washing it with soap and rinsing with water. We could not obtain the surface wettable with water by rubbing it with the finger tip in a stream of tap water. This is, probably, caused by the adsorption in monomolecular layer of soap molecule on the metallic surface, orientating the hydrocarbon group outward and anchoring the metal atom to the surface. We have cleaned the surface in the following manner.

The silver surface was polished, at first, with rouge-paper and flannel, and then washed electrolytically by electrolysing the mixture of the equal volumes of one per cent solutions of caustic soda and alcohol. The electrolytic cell consisted of platinum anode and silver cathode. The electrolysis was conducted at 6 volts and 0.1–0.2 ampere, being continued for 30–60 minutes. The surface of cathode was cleaned by the discharge of hydrogen on it. After such a treatment, the surface was rinsed with distilled water and then with drains of distilling alcohol for one hour by hanging the plate at the outlet of the condenser tube of the distillation apparatus. It was dried in a desiccater by passing a current of dry air. The silver plate cleaned by such a manner was readily wetted with water, alcohols, organic acids and hydrocarbons. The surfaces of glass and silver were cleaned by the above manner before each measurement.

Friction Coefficients of Pure Liquids.

The liquids tested were of possible purity and were dehydrated and fractionally distilled before the experiment. The aliphatic hydrocarbons, such as hexane, usually contain some unsaturated hydrocarbons as impurities. These impurities

7) W. B. Hardy and I. Doubleday, *Proc. Roy. Soc.*, A100, 550 (1922).

can not be removed merely by distillation. The sample containing these impurities gives somewhat lower friction coefficients. The hydrocarbon used in the present experiments was purified by shaking with fuming sulphuric acid for several days, dried over metallic sodium and then distilled. The sample of glycerol was obtained by fractionating several times under reduced pressure and then crystallizing.

The observed friction coefficients of various liquids for glass on glass and silver on silver are given in Table I.

Table I.

Static friction coefficients of pure liquids.

Liquid		Friction coefficient for glass on glass	silver on silver
No liquid (clean surfaces)		1.04	1.04
Water	H_2O	0.90	0.91
Methyl alcohol	CH_3OH	0.79	0.90
Ethyl alcohol	C_2H_5OH	0.72	0.88
n-Propyl alcohol	$CH_3(CH_2)_2OH$	0.64	0.84
n-Butyl alcohol	$CH_3(CH_2)_3OH$	0.60	0.76
n-Amyl alcohol	$CH_3(CH_2)_4OH$	0.57	0.65
n-Hexyl alcohol	$CH_3(CH_2)_5OH$	—	0.66
n-Heptyl alcohol	$CH_3(CH_2)_6OH$	—	0.56
n-Cetyl alcohol	$CH_3(CH_2)_7OH$	0.53	0.53
Acetic acid	CH_3COOH	0.60	0.91
Propionic acid	CH_3CH_2COOH	0.58	0.84
Butyric acid	$CH_3(CH_2)_2COOH$	0.59	0.71
n-Valeric acid	$CH_3(CH_2)_3COOH$	0.61	0.59
n-Caproic acid	$CH_3(CH_2)_4COOH$	0.59	0.54
n-Heptylic acid	$CH_3(CH_2)_5COOH$	0.62	0.45
Caprylic acid	$CH_3(CH_2)_6COOH$	0.53	0.31
Nonylic acid	$CH_3(CH_2)_7COOH$	0.57	0.27
Methyl acetate	CH_3COOCH_3	0.87	—
Ethyl acetate	$CH_3COOC_2H_5$	0.81	0.82
n-Propyl acetate	$CH_3COOC_3H_7$	0.81	0.73
n-Butyl acetate	$CH_3COOC_4H_9$	0.78	0.68
n-Amyl acetate	$CH_3COOC_5H_{11}$	0.74	0.68
n-Octyl acetate	$CH_3COOC_8H_{17}$	0.73	0.62
Ethyl propionate	$C_2H_5COOC_2H_5$	0.80	0.83
Ethyl butylate	$C_3H_7COOC_2H_5$	0.80	0.77
Methyl salicylate	$C_6H_4OHCOOCH_3$	0.69	—

Acetone	$(CH_3)_2CO$	0.86	—
Methyl ethyl ketone	$CH_3COC_2H_5$	0.83	—
Diethyl ketone	$C_2H_5COC_2H_5$	0.84	—
Acetophenone	$C_6H_5COCH_3$	0.73	—
n-Hexane	$CH_3(CH_2)_4CH_3$	0.85	0.96
n-Heptane	$CH_3(CH_2)_5CH_3$	—	0.94
n-Octane	$CH_3(CH_2)_6CH_3$	—	0.97
n-Nonane	$CH_3(CH_2)_7CH_3$	0.76	—
Benzene	C_6H_6	0.78	0.97
Toluene	C_7H_8	0.76	—
n-Xylene	C_8H_{10}	0.76	—
Glycerol	$(CH_2OH)_3$	0.86	—
Oleic acid	$C_{17}H_{33}COOH$	0.29	0.24

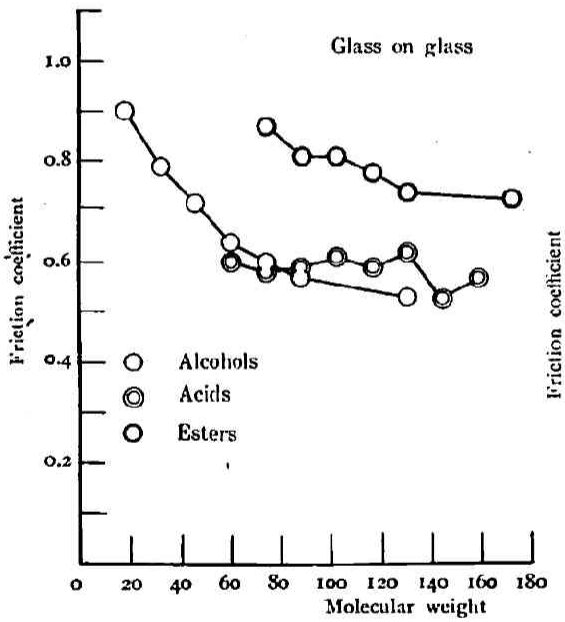

Fig. 3.

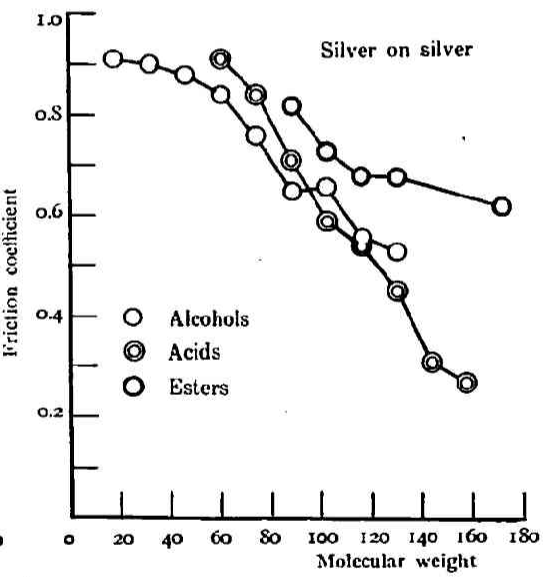

Fig. 4.

In Fig. 3 and 4 the friction coefficients are plotted against the molecular weight of the liquid. From these values we see that the friction for glass on glass is not affected much by the change of the molecular weight of the liquid, while that for silver on silver changes remarkably with the molecular weight. The friction between silver surfaces decreases by the increase in the moleculer weight of the member in a homologous series.

This fact may be explained by the affinity of the liquid molecule and the surface. The molecule of alcohol, acid or ester has small affinity to glass surface,

but great affinity to silver surface. So the molecules orientate more regularly on silver than glass, the polar group being attached to the solid surface. In this case, the longer molecule may arrange more regularly than the shorter one, and, therefore, the liquid of high molecular weight has small friction coefficient.

Glycerol shows relatively large friction, which indicates that the viscosity of liquid has no significance on the boundary friction. The hydrocarbons have large friction coefficients both for glass on glass and for metal on metal. This may be explained by the fact that the hydrocarbon molecules have no polar group, and, therefore, they take no orientation on the surface, or they hardly make a film between the surfaces. If the sample of hydrocarbon contains a minute quantity of polar substance as impurity, then the friction is lowered considerably. The purest sample must be used for the measurement. The polar substance is adsorbed selectively on the solid surface and shows profound effect on the friction. This fact was proved by the following experiments.

Friction Coefficients of Solutions.

The static friction coefficients for glass on glass have been measured of the solution of polar substance in nonpolar solvent. For example, oleic acid in toluene or palmitic acid in m-xylene etc. The results are shown in Table II and Fig. 5.

Table II.

Friction coefficients of dilute solutions for glass on glass

Solvent	Solute	Concentration of solute per cent	Friction coefficient
Pure toluene	—	—	0.76
Toluene	Oleic acid	0.05	0.53
		0.1	0.43
		0.5	0.36
		1.0	0.38
		2.0	0.35
—	Pure oleic acid		0.29
Pure m-xylene	—	—	0.76
m-Xylene	Palmitic acid	0.1	0.48
"		0.5	0.31
		1.0	0.29
		2.0	0.31
		4.0	0.32
Pure n-nonane	—	—	0.76
n-Nonane	Palmitic acid	2.0	0.31

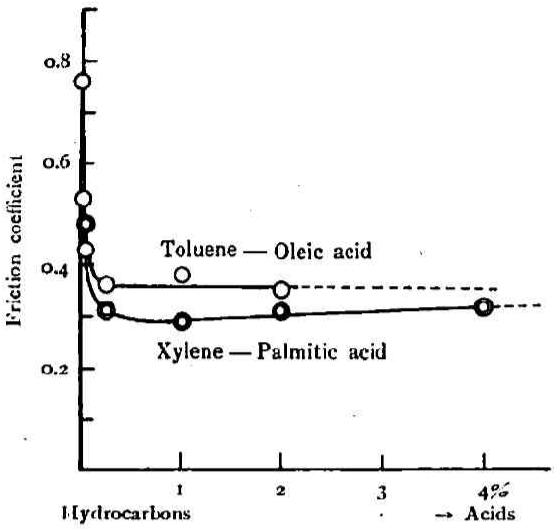

Fig. 5.

In the practical engineering, a patent "germ process" by Wells and Southcombe[8] depends on the fact that the addition to mineral oil of small percentage of such compounds as fatty acids that lower the interfacial tension between water and oil gives exceptionally good lubricating values.

It may be said that, in boundary lubrication, the friction depends only upon the adsorbed layer, and the other part of the solution does not impart the friction or oiliness. Such an adsorption, however, will be a dynamical equilibrium between the solid surface and the liquid in mass, so the orientation of the molecules will not be so complete as that deposited by Blodgett's method. It is natural, therefore, that the friction of the former is much greater than the latter. This fact has been proved experimentally in our laboratory and will be shown later.

The same idea as above may be extended to the case when the solvent is also polar, but the phenomena are more complicate. The addition of a small quantity of a fatty substance is not effective generally. The results are shown in Table III and Fig. 6.

We see, from Fig. 6, that the friction coefficient of the mixtures of oleic acid and acetic acid, as well as water and acetic acid, is nearly equal to

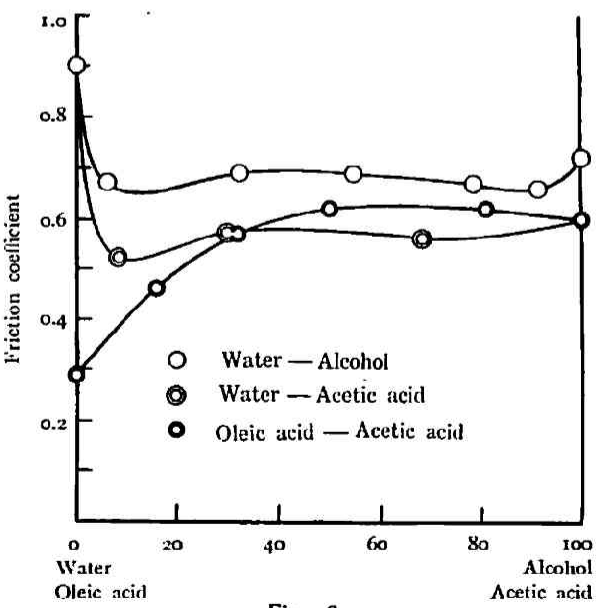

Fig. 6.

8) H. M. Wells and J. E. Southcombe, *J. Soc. Chem. Ind.*, 39, 51 T (1920).

Table III.

Friction coefficients of mixtures for glass on glass

Component 1	Concentration per cent	Component 2	Concentration per cent	Friction coefficient
—	—	pure acetic acid	100	0.60
Oleic acid	19	acetic acid	81	0.62
	50		50	0.62
	68		32	0.57
	84		16	0.46
Pure oleic acid	100	—	—	0.29
—	—	pure acetic acid	100	0.60
Water	31.6	acetic acid	68.4	0.56
	70		30	0.57
	92		8	0.52
Pure water	100	—	—	0.90
—	—	pure ethyl alcohol	100	0.72
Water	8.4	ethyl alcohol	91.6	0.66
	21.2		78.8	0.67
	45.3		54.7	0.69
	67.6		32.4	0.68
	94.0		6.0	0.67
Pure water	100	—	—	0.90

that of the latter component when acetic acid exceeds 30 per cents in amount. This indicates that the acetic acid is adsorbed on glass surface preferentially. There are, however, many unknown factors affecting the friction and the quantitative discussion cannot be done so far.

It is a well known fact that the mixture of water and alcohol has a maximum viscosity. There is found no such maximum in the curve of friction coefficient, which is another proof of the independence of viscosity and boundary friction.

Friction Coefficient, Sedimentation Volume and Thixotropy.

We have measured the sedimentation volumes of powders, the glass powder for example, in liquids, and found that the powder has larger sedimentation volume in a nonpolar liquid than in a polar one[9]. If, however, a minute quantity of fatty substance is added to the nonpolar solvent, then the sedimentation volume decreases remarkably. The change of the sedimentation volume of the glass powder in toluene by the addition of oleic acid is shown in Table IV and Fig. 7.

9) H. Akamatu, *Bull. Chem. Soc. Japan*, 13, 456 (1938).

Table IV.

Sedimentation volume of glass powder in toluene

Concentration of oleic acid in toluene per cent	Sedimentation volume (relative value)
0 (pure toluene)	1.00
0.02	0.90
0.1	0.85
0.5	0.79
1.0	0.79
1.9	0.78

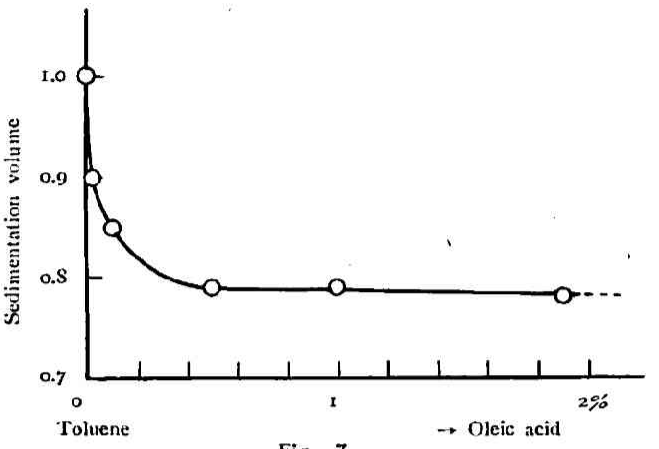

Fig. 7.

Thus the curve of sedimentation volume (Fig. 7) is of quite the same form with the curve of friction coefficient (Fig. 5). The oleic acid is selectively adsorbed on the surfaces of glass powders, and "lubricate" them, so that the powders slide each other and finally settle in the state of close packing.

It can generally be said that there is the parallelism between the large sedimentation volume and thixotropic nature, for both of these phenomena occur by the loose packing of a system. But a small quantity of fatty substance is added to such a system, then the thixotropic nature is entirely destroyed. For example, the mixture of glass powder with toluene is distinctly thixotropic, which, however, becomes non-thixotropic by the addition of 1 per cent of oleic acid. This can be explained as the result of lubrication of the glass surface by the adsorption of oleic acid.

Friction Coefficients of Monomolecular Films.

Hardy found that the value of the coefficient of friction is practically independent of the quantity of the lubricating liquid, or the thickness of the film of liquid[9]. Langmuir devised a method of depositing monomolecular film of oleic acid on a glass plate[10] which then was improved by Blodgett and was made possible to deposit succesive layers of fatty acid on a solid surface[11].

Let a small quantity of fatty acid spread on the surface of water making monomolecular film. The area of the film is confined by using a boundary thread and a "piston oil". Now a glass plate is dipped edgewise in such a water and

10) I. Langmuir, *Trans. Farad. Soc.*, 15, 68 (1920).

11) K. B. Blodgett, *J. Am. Chem. Soc.*, 57, 1007 (1935).

withdrawn slowly, then a monomolecular film of fatty acid will be deposited on the glass plate. If the process is repeated once more, then the plate is covered with three molecular layers and so on.

By this method, we have made the film of known thickness on a glass plate, and have measured the coefficient of static friction of such a glass surface. The tap water was used for the underlying water of monomolecular floating film, the hydrogen ion concentration of which is pH=7.8 and contains some calcium ion. Some examples of the experimental results under various conditions are given in Table V.

Table V.

Friction coefficient for glass on glass in the presence of stearic acid film

Surface of plate	Surface of slider	Friction coefficient
Clean glass	Clean glass	1.04
Glass covered with the film of stearic acid of 1-molecular layer	Clean glass	0.11
The same of 3-molecular layer	Clean glass	0.12
Clean glass	Glass covered with the film of stearic acid of 1-molecular layer	0.34
Glass covered with the film of stearic acid of 1-molecular layer	Glass covered with the film of stearic acid of 1-molecular layer	0.11

We see, from Table V, that the friction is somewhat larger when the slider is covered with film and the plate is clean than the case of the clean slider and covered plate. The slider surface is in contact with the plate at a very small area if not at a point. So the monomolecular film of stearic acid on the slider is liable to be torn off at this contact point, and in consequence of this the friction becomes large. It is necessary, therefore, to deposit the film on the surface of plate in the study of the friction of films.

The results of the measurements are summarized in Table VI. The data in this table have been obtained when the surface of plate is covered with the monomolecular film of the substances, the slider surface being clean. The "piston oil" used in the deposition of the film is also shown in the table.

From Table VI we see that there are little differences of the coefficients of friction among these substances, provided that the thickness of film is one-molecular. If the "piston oil" is changed from castor oil to oleic acid, there occurs, generally, a small change in the friction coefficient. Castor oil gives larger value of friction than oleic acid. This may be explained by the fact that oleic acid has greater surface pressure (about 30 dynes) than castor oil (about 17 dynes), so the former deposits the film in more compressed state than the latter,

Table VI.

Friction coefficient for glass on glass in the presence of monomolecular film.

Film substance	"Piston oil"	
	Castor oil	Oleic acid
Stearic acid	0.12	0.10
Palmitic acid	0.13	0.10
Myristic acid	0.20	0.11
Lauric acid	0.18	0.18
Oleic acid	0.20	0.14
Ricinoleic acid	0.15	0.12
Tripalmitine	0.14	—

Table VII.

Friction coefficient for glass on glass in the presence of mono- and poly-molecular film

Thickness of the film	Palmitic acid film	Oleic acid film
No film (clean glass)	1.04	1.04
1-Molecular layer	0.10	0.14
3-Molecular layer	0.09	0.10
5-Molecular layer	0.07	0.16
7-Molecular layer	0.06	0.15
9-Molecular layer	0.06	0.18
11-Molecular layer	0.07	—

Relatively large difference of friction is detected by the change of "piston oil" in the case of myristic acid. Myristic acid makes an expanded film and the compressibility of the film is larger than other substances which make the condensed film.

The friction coefficients of the films thicker than three-molecular layer are given in Table VII. The measurements have been done on palmitic acid and oleic acid. Oleic acid has been used for the "piston oil" in the deposition of the films.

This table shows that there is almost no change in the value of the friction coefficient in spite of the change of thickness of the film. The presence of the film of only one molecular layer reduces the friction coefficient to about one tenth of the clean glass surface, but almost no further reduction takes place by the increase of the thickness of film. This is a remarkable fact. In the film deposited by Blodgett's method, all of the oil molecules take the vertical position on the glass surface. The polar group of the oil molecule contacts with the surface of glass, and the nonpolar hydrocarbon group directs to the air. It is possible that such a regular arrangement of molecules favours the lubricating power more than the irregular arrangement. We can deposit the film on glass surface by means of the condensation of vapour or the evaporation of solvent from the solution. These methods, however, give less regular arrangement of molecules than Blodgett's method. The friction coefficient of oleic acid was measured to be about 0.3 in the case of the film deposited by the evaporation of the benzene solution. It was already reported that the friction coefficient of oleic acid is 0.29 when the glass surface is flooded with the liquid oil. Thus we see that the regular arrangement of oil molecules gives smaller friction coefficient than the irregular arrangement.

Summary.

The method of measuring the static boundary friction coefficient has been described. The friction coefficients have been measured of alcohols, organic acids, esters, hydrocarbons, etc. for glass on glass and for silver on silver, as well as of binary solutions of some organic substances for glass on glass. The friction of organic liquid in one homologous series decreases with the increase of the molecular weight, especially in the case of silver surfaces. In the solution of fatty acid in hydrocarbon, the friction only depends upon the solute and not the solvent. The selective adsorption of polar substance to the glass surface may account for this fact. The sedimentation volume and the thixotropic nature of powder are in some relations with the friction coefficient.

The friction coefficients have been measured of mono- and poly-molecular films of fatty acids on glass. The presence of the monomolecular film of a fatty acid reduces the friction to about one tenth of the clean glass surface, but no further reduction takes place by the increase of the thickness of the film. The regular arrangement of oil molecules gives smaller friction coefficient than the irregular arrangement.

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